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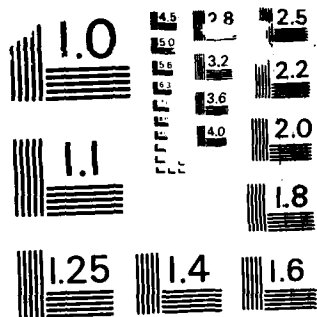
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REPORT NO. NADC-84167-60

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PORPHYRINS AS CORROSION INHIBITORS

Frederick R. Longo
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Philadelphia, PA 19104

JULY 1984

FINAL REPORT
Contract No. N62269-81-C0278

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Prepared For
NAVAL AIR DEVELOPMENT CENTER
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ADA 157 621

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Drexel University
Philadelphia, PA

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SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE				
1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS ADA 157 621	
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for Public Release; Distribution Unlimited	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			5. MONITORING ORGANIZATION REPORT NUMBER(S)	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) NADC-84167-60				
6a. NAME OF PERFORMING ORGANIZATION Drexel University		6b. OFFICE SYMBOL (If applicable)		7a. NAME OF MONITORING ORGANIZATION
6c. ADDRESS (City, State, and ZIP Code) Philadelphia, PA 19104			7b. ADDRESS (City, State, and ZIP Code)	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Naval Air Development Center		8b. OFFICE SYMBOL (If applicable)		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N62269-81-C-0278
8c. ADDRESS (City, State, and ZIP Code) Warminster, PA 18974			10. SOURCE OF FUNDING NUMBERS	
			PROGRAM ELEMENT NO.	PROJECT NO.
			TASK NO.	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) PORPHYRINS AS CORROSION INHIBITORS				
12. PERSONAL AUTHOR(S) Frederick R. Longo				
13a. TYPE OF REPORT Final		13b. TIME COVERED FROM 7-1-81 TO 8-31-83		14. DATE OF REPORT (Year, Month, Day) 1984 July
				15. PAGE COUNT 55
16. SUPPLEMENTARY NOTATION				
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP		
			Corrosion - Porphyrins - Metalloporphyrins - Potentiostatic polarization - Corrosion Inhibitors - Corrosion Inhibition	
19. ABSTRACT (Continue on reverse if necessary and identify by block number)				
<p>The porphyrin molecule is a Lewis acid with four nitrogen donor atoms at its core. It is therefore a strongly-bonding tetradentate chelating agent.</p> <p>If corrosion inhibition depends on the inhibitor's ability to form bonds with atoms (metal atoms/ions or oxygen-oxygen atoms) it seems reasonable to examine the changes in corrosion potential and corrosion rate brought about by treatment of metallic surfaces with various porphyrins and metalloporphyrins because the porphyrins can form strong bonds to a surface by several chemical mechanisms.</p> <p>In this contract period our project on inhibition of corrosion by porphyrins had three aspects: (1) Preparation of materials, (2) corrosion rate studies, and (3) potentiostatic polarization studies.</p> <p>We have synthesized over forty different porphyrins and metalloporphyrins for the study. Our corrosion rate and potentiostatic studies indicate that porphyrins change the processes occurring at the corrosive solution/metal interface. In this final report we discuss the synthesis and testing of the porphyrins and metalloporphyrins. The water soluble porphyrins seem most promising. On the basis of our experience we plan to synthesize several highly charged (+8) cationic porphyrins for further study. We also intend to examine porphyrin-treated iron surfaces by electron microscopy.</p>				
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT			21. ABSTRACT SECURITY CLASSIFICATION	
<input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS				
22a. NAME OF RESPONSIBLE INDIVIDUAL Frederick R. Longo			22b. TELEPHONE (include Area Code) (215) 441-2291	
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TABLE OF CONTENTS

	<u>Page</u>
1.0 INTRODUCTION	1
2.0 SYNTHESIS OF MATERIALS	8
2.1 Preparation of Porphyrin	8
2.1.1 Tetraarylporphins	8
2.1.2 Porphin	9
2.1.3 Bromo and Nitro Porphins.	10
2.2 Purification of the Porphyrins	12
2.3 Characterization of the Porphyrins	13
2.4 Preparation of Metalloporphyrins	13
2.4.1 Incorporation of Mn(II)	13
2.4.2 Incorporation of Zn(II), Co(II), Ni(II), and Cu(II).	
2.4.3 Incorporation of Cr(II)	14
2.4.4 Incorporation of Fe(III).	14
2.4.5 Incorporation of Vanadyl, VO(II).	15
2.5 Purification of Metalloporphyrins.	15
3.0 DIRECT CORROSION STUDIES; MASS LOSS RATES.	15
3.1 Procedure.	15
3.2 Results.	16
4.0 POTENTIOSTATIC POLARIZATION STUDIES.	19
4.1 Apparatus.	19
4.2 Procedures	23
4.3 Results.	24

TABLE OF CONTENTS

	<u>Page</u>
5.0 DISCUSSION	33
6.0 ACKNOWLEDGEMENTS	34
7.0 REFERENCES	35
8.0 APPENDIX	37

Document 1: On the Aromaticity of porphin, L.R. Nudy, J.C. Coffey, F.R. Longo and J.B. Kim. J. Heterocyclic Chem, 19:1589 (1982).

Document 2: A Study of the Bromoporphins, L.R. Nudy, H.G. Hutchinson, C. Schieber and F.R. Longo. Tetrahedron, 40:2359 (1984).

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1. A list of all metal-free porphyrins prepared for corrosion inhibition testing	2
2. A list of all metalloporphyrins prepared for corrosion inhibition testing	7
3. Synthesis of Porphin	11
4. Results of Corrosion Studies	17
5. Results of weight-loss tests using ms-tetramethylpyridylporphin with various counter-anions	20
6. Corrosion Rates in the Presence of Metalloporphyrins concentration of porphyrin: $10^{-4}M$	21
7. The Effect of the Variation of Porphyrin Concentration and Environment on the Rate of Corrosion	22

LIST OF ILLUSTRATIONS

<u>Figure</u>	<u>Page</u>
1. The aromatic pathway in porphin.	12
2. A comparison of the potentiostatic polarization curves using a pure iron working electrode and a 401 steel working electrode in 2.0% NaCl(aq) with no inhibitor	26
3. The potentiostatic polarization curve using a pure iron working electrode in 2.0% NaCl(aq), containing ms-tetramethylpyridylporphin ($10^{-4}M$) as an inhibitor	27
4. The potentiostatic polarization curve using a pure iron working electrode in 2.0% NaCl(aq), containing vanadyl-ms-tetramethylpyridylporphin ($10^{-4}M$) as an inhibitor	28
5. The potentiostatic polarization curve using a pure iron working electrode in 2.0% NaCl(aq), containing iron(III)-ms-tetramethylpyridylporphin ($10^{-4}M$) as an inhibitor	29

LIST OF ILLUSTRATIONS

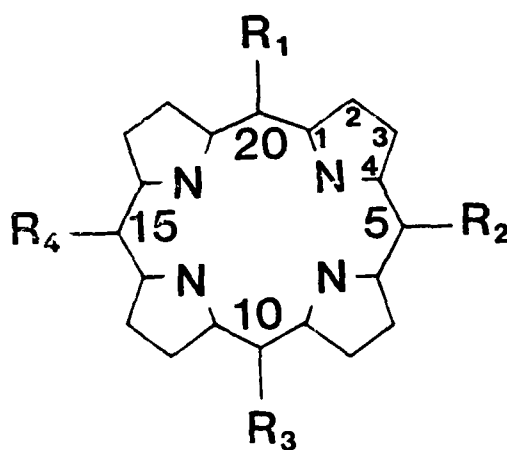
<u>Figure</u>	<u>Page</u>
6. The potentiostatic polarization curve using a pure iron working electrode in 2.0% NaCl(aq), containing Cu(II)-ms-tetramethylpyridylporphin ($10^{-4}M$) as an inhibitor	30
7. The potentiostatic polarization curve using a pure iron working electrode in 2.0% NaCl(aq), containing Co(II)-ms-tetrapethylpyridylporphin ($10^{-4}M$), as an inhibitor.	31
8. The potentiostatic polarization curve using a pure iron working electrode in 2.0% NaCl(aq), containing ms-tetracarboxyphenylporphin ($10^{-4}M$) as an inhibitor.	32

1.0 INTRODUCTION

A consideration of the chemical nature of porphyrins suggests that these species would interact strongly with metallic surfaces. The porphyrins can form strong bonds to a surface in at least five different ways: chelation of surface atoms by the four inner nitrogen atoms;¹ coordination of surface atoms by polar substituents at the porphyrin periphery; coordination of a surface atom to the central metal of a metalloporphyrin; "sitting atop" complex formation involving the porphyrin and a surface metal ion;^{2,3,4} and by interaction between the pi molecular orbitals of the porphyrin with the d-orbitals of the metal.⁵ In view of the kinds of chemical forces which affect porphyrin-surface interaction, we designed and synthesized structures which have inhibition potential. A list of these structures is presented in Tables 1 and 2. Most of these structures have been previously reported, but a few are new. We had difficulty in following many of the published procedures and in these cases we have developed modified techniques. In order to make our approach systematic we have attempted to synthesize porphyrins to which are bonded substituents of widely varying polarity so that we should see a wide range of interaction strength with metallic surfaces.

Table 1

A list of all metal-free porphyrins prepared for corrosion inhibition testing.



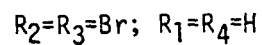
PORPHYRIN

- | | |
|---------------------------|-------------------------|
| 1. Porphin (Ref 6) | $R^*=H$ |
| 2. 2-Bromoporphin (Ref 7) | $R^*=H$ |
| 3. 5-Bromoporphin (Ref 6) | $R_2=Br; R_1=R_3=R_4=H$ |

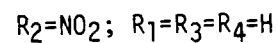
*In cases where $R_1=R_2=R_3=R_4$ we use R

Table 1 (Continued)

4. 5,10-dibromoporphin (Ref 6)



5. 5-nitroporphin (Ref 8)



6. 5,10,15,20-tetraphenylporphin (Ref 9)

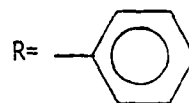
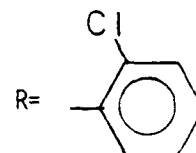
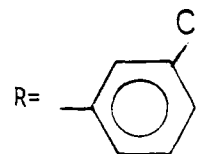
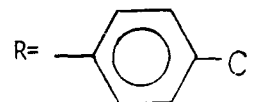
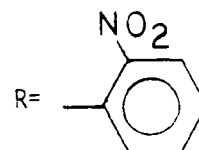
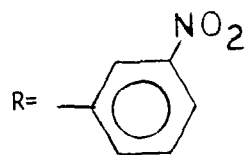
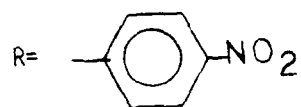
7. 5,10,15,20-tetra(o-chlorophenyl)porphin
(Ref 10)8. 5,10,15,20-tetra(m-chlorophenyl)porphin
(Ref 10)9. 5,10,15,20-tetra(p-chlorophenyl)porphin
(Ref 10)10. 5,10,15,20-tetra(o-nitrophenyl)porphin
(Ref 10)

Table 1 (Continued)

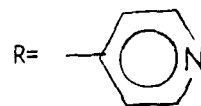
11. 5,10,15,20-tetra(m-nitrophenyl)porphin
(Ref 10)



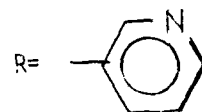
12. 5,10,15,20-tetra(p-nitrophenyl)porphin
(Ref 10)



13. 5,10,15,20-tetra(4-pyridyl)porphin
(Ref 11)



14. 5,10,15,20-tetra(3-pyridyl)porphin
(Ref 12)



15. 5-(4-carboxyphenyl)porphin
(Ref 13)

$R_1=R_2=R_3=H$;

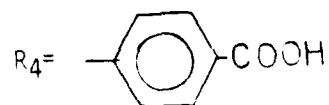


Table 4. Results of Corrosion Studies (Continued)

<u>Sample</u>	<u>Porphyrin Solution</u>	<u>%Δm, 12 h</u>	<u>%Δm, 48 h</u>
14.	T(o-ClP)P/Tenzone	---	5.88
15.	Fe ^{III} TPPCl/Benzene	1.57	---
16.	Fe ^{III} TPPCl/Benzene	---	6.37

B. Temperature of Porphyrin Treatment (Reflux)

<u>Sample</u>	<u>Porphyrin Solution</u>	<u>%Δm, 12 h</u>	<u>%Δm, 48 h</u>
1.	TPP/Benzene	1.81	---
2.	TPP/Tenzone	1.72	---
3.	TPP/Benzene	---	7.63
4.	T(o-ClP) Benzene	1.66	---
5.	T(o-ClP)P/DMF	---	0.22
6.	T(o-ClP)P/DMF	---	0.47

Table 4
Results of Corrosion Studies

A. Temperature of Porphyrin Treatment, 20-22°C

<u>Sample</u>	<u>Porphyrin Solution</u>	<u>%Δm, 12 h</u>	<u>%Δm, 48 h</u>
1.	Untreated (Blank) ^a	1.44	
2.	Untreated (Blank)	1.72	
3.	Untreated (Blank)	---	6.81
4.	Untreated (Blank)	---	6.23
5.	Pure solvent (Blank) ^b	1.53	---
6.	Pure solvent (Blank)	1.34	---
7.	Pure solvent (Blank)	---	6.12
8.	Pure solvent (Blank)	---	6.01
9.	TPP/Benzene	1.66	---
10.	TPP/Benzene	1.77	---
11.	TPP/Benzene	---	6.93
12.	T(o-C1P)P/Benzene	1.42	---
13.	T(o-C1P)P/Benzene	1.13	---

a. Iron specimen was buffed, weighed and immersed in test environment.

b. Iron specimen was buffed, immersed in pure solvent, dried, weighed and immersed in test environment.

methods depending on the water solubility of the porphyrins. For water insoluble porphyrins the iron samples were carefully polished and then immersed in a solution of the porphyrin in an organic solvent, either benzene or N,N-dimethylformamide (DMF). The samples were immersed at ambient and also at reflux temperatures. (80°C for benzene and 140°C for DMF). These samples were removed from the solution, rinsed with pure solvent and dried at 50°C for one hour. The specimens were then completely immersed in corrosive environments, either 1.00% aqueous NaCl or 1.00% aqueous NaCl of pH 4.

3.2 Results

Generally, corrosion was obvious in almost all cases within 1 to 1.5 hours. The results of these studies on water insoluble porphyrins are presented in Table 4. It is to be noted that no samples showed corrosion rates significantly different from untreated samples except samples B5 and B6. These samples were treated with refluxing solutions of 5,10,15,20-tetra-(o-chlorophenyl) porphin in DMF.

Table 4 reports the %-loss in mass at 12 and 48 hours. These percentages are proportional to corrosion rates which can be calculated from our data. We have estimated that the corrosion rate for iron is approximately 490mg/d. dm^2 or 0.09 ipy. This is considered as fairly rapid and unsatisfactory⁴.

Inasmuch as many successful inhibitors are ionic we have prepared and tested ionic, water soluble porphyrins and water soluble metalloporphyrins. We have made many chemical modifications of 5,10,15,20-tetra-4-pyridylporphin, structure #13 in Table 1. Treatment with methyl iodide converts #13 into an ionic methylated derivative which is water soluble^{21,22}, structure #24, Table 1.

(pH 4) to remove the traces of unreacted porphyrin.

2.4.5 Incorporation of vanadyl, VO(II)

The incorporation of vanadyl is extremely slow by most methods. For example, using a 50-fold molar excess of vanadyl sulfate (VOSO_4) to porphyrin (1g per 500ml) in refluxing DMF, fluorescence, indicating that incorporation was incomplete, was observable even after three weeks of continuous refluxing. In some cases it is possible to use vanadium tetrachloride, VCl_4 , to prepare the vanadyl porphyrin. This method was effective for the metallation of ms-tetra-4-pyridylporphin. The porphyrin (500mg) is heated with the neat, liquid VCl_4 (50ml) at 165°C for 4 hours. After cooling the excess VCl_4 is allowed to evaporate. The product is then dissolved in hot benzene from which it crystallizes upon cooling to room temperature.

2.5 Purification of Metalloporphyrins

The chief impurities in the metalloporphyrins are solvent from the metalloporphyrin preparation reaction and traces of unreacted, free-base porphyrin. Both impurities are removed by the chromatographic method described above for the purification of the free-base porphyrins. Final purification is accomplished by forced crystallization from CHCl_3 using methanol.

3.0 DIRECT CORROSION STUDIES; MASS LOSS RATES

3.1 Procedure

In these studies we followed the techniques described by Pourbaix.¹⁶ For this work we used pure (99.99%) iron foil supplied by Armco. The test samples measure 2.8cm by 1.0cm. The tests were conducted by two different

refluxed in acetic acid until the reaction mixture no longer fluoresces under a violet-light; this indicates the complete conversion of the free base porphyrin into the corresponding metalloporphyrin. The yield is 90%. The Mn^{II} -porphyrins are easily oxidized to Mn^{III} -porphyrins.

2.4.2 Incorporation of Zn(II), Co(II), Ni(II) and Cu(II)

The porphyrin (2.50g) and the metal chloride salt, MCl_2 (10.00g) are refluxed in 1.00 liter of DMF until fluorescence is quenched or until spectrophotometric analysis indicates the collapse of the four-banded visible spectrum into a two-banded visible spectrum. Both observations signal the conversion to the metalloporphyrin. The yields are generally from 80 to 90%.

2.4.3 Incorporation of Cr(II)

The porphyrin (1.5g) and chromium carbonyl $Cr(CO)_6$ (5g) are suspended in 1.00 liter of decalin and refluxed under a nitrogen atmosphere for 5-6 hours. The solvent and unreacted $Cr(CO)_6$ are removed under reduced pressure, the residue is dissolved in toluene, and the porphyrin is precipitated by addition of n-pentane or n-heptane.

2.4.4 Incorporation of Fe(III)

A 0.1M solution of Fe(II) acetate in glacial acetic acid is added to a solution of the porphyrin (1.00g) in refluxing acetic acid. Conversion to the Fe(II) porphyrin is virtually immediate and the oxidation to the Fe(III) porphyrin acetate is complete after 5 minutes. Addition of NaCl causes the crystallization of the Fe(III) porphyrin chloride (hemin) on cooling. This product is soluble in ether, in which medium it can be washed with aqueous HCl

alumina. A column approximately 2.5cm in diam. by 30cm in length is packed with alumina and a concentrated solution of crude porphyrin is layered onto the column. Elution is carried out with acid-free chloroform. Fractions with the same visible spectrum are combined, concentrated and rechromatographed. Acceptable fractions from the second chromatography are again combined. The addition of methanol forces the porphyrins to crystallize from the chloroform solution. In this manner we generally obtain 25 to 30mg of pure porphyrin from an original 50mg charge of crude. (50 to 60% recovery).

2.3 Characterization of Porphyrins

The structures of the new porphyrin compounds were proved by chemical analysis, mass spectrometry, and proton Fourier transform nuclear magnetic resonance. The previously reported compounds which we prepared for use in these studies were characterized by visible absorption spectroscopy.

2.4 Preparation of Metalloporphyrins

There is no general procedure for the conversion of porphyrins to metalloporphyrins. This is primarily due to the fact that the reactants, the porphyrin and the metal salt, are generally insoluble in the same medium: Porphyrins are soluble in non-polar solvents and metal salts are soluble in polar solvents. Microemulsion media, N,N-dimethylformamide (DMF), and acetic acid can be used to circumvent this general problem since all three media are capable of solubilizing ionic and non-ionic substances.

2.4.1 Incorporation of Mn(II)

The porphyrin (1.00g), MnCl_2 (10.0g) and sodium acetate (1.00g) are

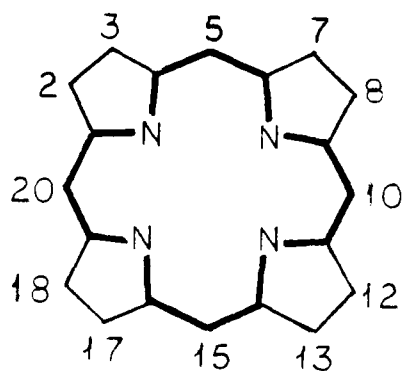


Figure 1

The aromatic pathway in porphin: dark bonds.

chemical modification or chemical substitution, is considered and when molecular orbital energies are to be calculated. Our studies of bromoporphins suggest that the theoretical calculations, which have been conducted assuming that all carbon atoms are equivalent,²³ should be repeated.

Enclosed in the Appendix are the manuscripts of two journal articles which describe the bromoporphin work.

2.2 Purification of the Porphyrins

The most effective technique for purification of these compounds was found to be column chromatography of concentrated chloroform solutions on dry

Table 3
Synthesis of Porphin

Moles of Reagents

<u>Dimethylol pyrrole</u>	<u>pyrrole</u>	<u>Solvent</u>	<u>Volume</u>	<u>Temp.</u>	<u>Time</u>	<u>Yield</u>
3.8×10^{-4}	3.8×10^{-4}	xylene	0.75	100	6 hrs.	2.0%
4.9×10^{-4}	3.0×10^{-3}	o-xylene	0.75	101	2.5 hrs.	3.5%
1.9×10^{-3}	2.1×10^{-3}	methanol	4.50	66	48 hrs.	none detected
5.1×10^{-5}	7.0×10^{-5}	p-xylene	0.10	90	47 hrs.	4.8%
5.1×10^{-5}	3.8×10^{-4}	p-xylene	0.10	90	22 hrs.	3.8%
5.2×10^{-5}	5.4×10^{-5}	cumene	0.10	98- 102	22 hrs.	3.8%
3.4×10^{-4}	6.8×10^{-4}	propanol	0.60	97	3 hrs.	none detected

However, 2,5-dimethylpyrrole¹⁹ and pyrrole are more easily obtained than 2-methylpyrrole.²⁰ A further advantage is that the latter synthesis of porphin can be accomplished in propionic acid solvent at room temperature. Longo et al.¹⁸ have found that porphin could not be synthesized from 2-methylpyrrole at temperatures lower than 80°C. Unfortunately, even under our conditions, the yield of porphin is too low at room temperature to make this a practical alternative. The results of attempted syntheses using the latter method are summarized in Table 3.

2.1.3 Bromo and Nitro Porphins

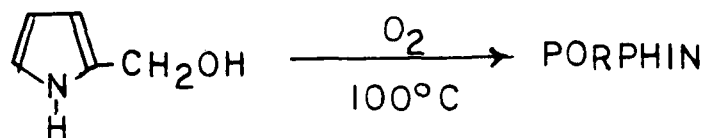
We have prepared bromo and nitro derivatives of porphin by methods which have been successful for bromination and nitration of benzene. The bromoporphins (entries 2, 3, and 4, Table 1) are especially important in terms of corrosion studies because of the ease with which these compounds can be converted to ionic or polar water-soluble materials by reaction with amines.

In addition the study of bromoporphins has led us to an extremely important conclusion regarding the electronic structure of the porphyrin skeleton. Our results indicate that aromatic character (i.e., benzene-like character) of porphin does not extend to the β -carbon atoms of the pyrrol residues (Atoms 2,3,7,8,12,13,17 and 18 in Figure 1). This means that the reactivity at the methine bridges (5,10,15,20) is different from the reactivity at the peripheral pyrrol carbon atoms, the same conclusion reached by Fleischer and Webb¹⁷ on the basis of an X-ray crystallographic study of porphin.

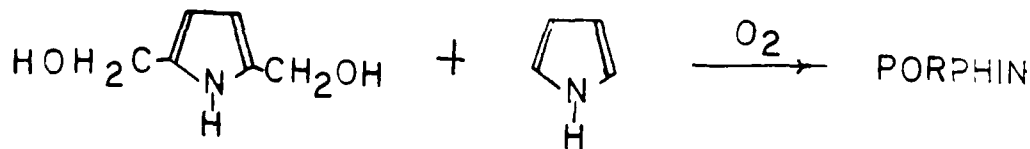
The difference in the behavior of the peripheral carbon atoms has both practical and theoretical implications which must be kept in mind when

2.1.2 Porphin

No preparation of the parent, unsubstituted porphyrin, which is called porphin, is satisfactory;¹⁸ the best yields reported to date are 18% by the condensation of pyrrole alcohol in xylenes at extremely high dilutions:



Under ordinary synthetic conditions the yield is more likely to be 8 to 10%. Until the synthesis of porphin is considerably improved it will not be feasible to investigate its device potential. Therefore, we examined a novel reaction for the preparation of this important compound; it involves the condensation of 2,5-dimethylolpyrrole with pyrrole under various conditions:

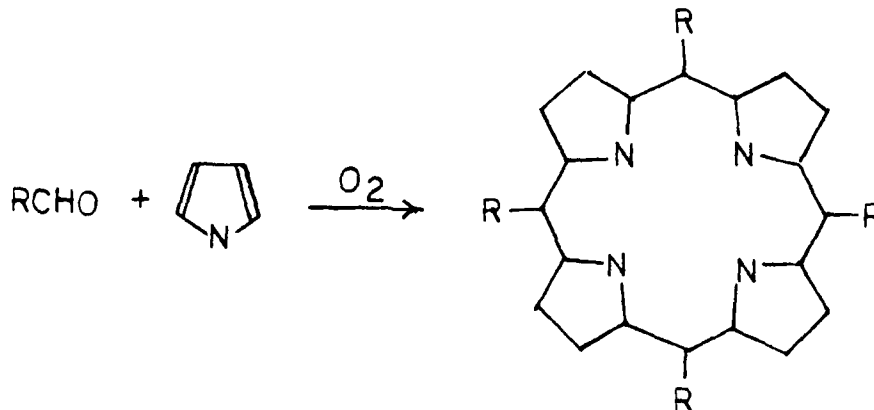


From the results of our studies we conclude that the novel method provides little or no advantages over the method utilizing 2-methylolpyrrole as starting material. In all experiments the yield of porphin obtained by our newly developed synthesis are lower than those reported by Longo et al.¹⁸

2.0 SYNTHESIS OF MATERIALS

2.1 Preparation of the Porphyrins2.1.1 Tetraarylporphins

Even though the main thrust of this research is the search for porphyrin corrosion inhibition, the greatest fraction of our time has been devoted to the preparation and purification of materials. Many of these compounds were synthesized by the general procedure of Adler, Longo, et al.⁹ It consists of condensing an aldehyde (RCHO) with pyrrole in refluxing propionic acid. The R-group of the aldehyde becomes the methine bridge substituent in the porphyrin:



The crude porphyrin is obtained by filtration of the cooled reaction mixture. In the case of Table 1 - entries 13, 14, 16, 17, and 24, the product porphyrin is appreciably soluble even after cooling the reaction medium and more tedious procedures are required for separation of product.

Table 2

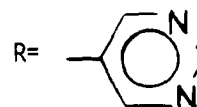
A list of all metalloporphyrins prepared for corrosion inhibition testing.

1. Derivatives of 5,10,15,20-tetraphenyl porphin; #6, Table 1
VO²⁺, Cr²⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺
2. Derivatives of 5,10,15,20-tetra-4-pyridylporphin; #13, Table 1
Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺
3. Derivatives of 5,10,15,20-tetra-(4-methylpyridyl)porphin; #24, Table 1
VO²⁺, Cr²⁺, Mn^{2+,3+}, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺

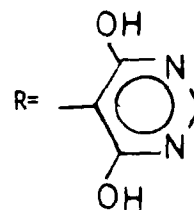
(In these studies iodide, I⁻, and toluene sulfonate, TS⁻, were most often used as counter-anions.)

Table 1 (Continued)

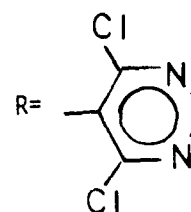
21. 5,10,15,20-tetra(5-pyrimidyl)porphin
(Ref 13)



22. 5,10,15,20-tetra(4,6-dihydroxy-5-pyrimidyl)porphin (Ref 13)

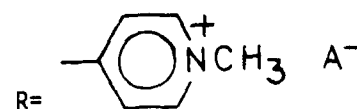


23. 5,10,15,20-tetra(4,6-dichloro-5-pyrimidyl)porphin (Ref 13)



24. 5,10,15,20-tetra(4-methylpyridyl)porphin,
A⁻ (Ref 21)

(A⁻ = Cl⁻, Br⁻, I⁻, 1/2SO₄²⁻, benzoate, benzene sulfonate)



25. 5,10,15,20-tetra(4-octylpyridyl)porphin iodide
(Ref 13)

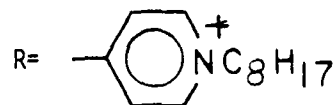
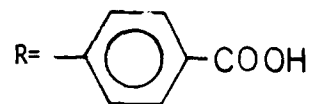
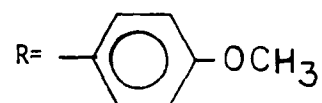


Table 1 (Continued)

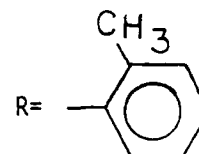
16. 5,10,15,20-tetra(4-carboxyphenyl)porphin
(Ref 14)



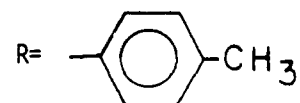
17. 5,10,15,20-tetra(4-methoxyphenyl)porphin
(Ref 10)



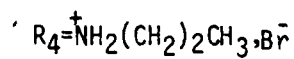
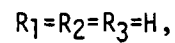
18. 5,10,15,20-tetra(o-methylphenyl)porphin
(Ref 10)



19. 5,10,15,20-tetra(p-methylphenyl)porphin
(Ref 10)



20. 5-porphinato-n-propylammonium bromide
(Ref 13)



The counter ion is iodide, but by ion exchange we also have synthesized the chloride, bromide, sulfate, and benzoate. By the reaction of structure #13 with methyl toluene sulfonate we also produced structure #24 with toluene sulfonate as counter ion. In this case the water solubility is very high. Table 5 summarizes the results of corrosion studies with structure #24 with the various counter ions. Surprisingly, the best results were obtained when chloride was the counter ion.

The metalloderivatives of 5,10,15,20-tetramethylpyridylporphin iodide (structure #24) showed definite inhibition relative to the metal free structures. The results of these studies are shown in Table 6. Note that all mass loss rates are lower than those obtained from metal free structures (Table 4) and that the Fe(III) derivative shows significant inhibition.

We have also performed tests to compare the effects of pH and porphyrin concentration on corrosion mass loss rates. In these studies we compared three different environments:

- A. Distilled water
- B. 1.0% aqueous NaCl solution
- C. 10^{-4} M HCl

Table 7 summarizes the results for 5,10,15,20-tetramethylpyridylporphin iodide, #24, Table 1. There is definitely a concentration effect but it is not noticeable in the presence of NaCl.

4.0 POTENTIOSTATIC POLARIZATION STUDIES

4.1 Apparatus

An electrochemical polarization cell modelled after cells used at NADC was constructed. It consisted of a two liter round bottom flask equipped with

Table 5

Results of weight-loss tests using ms-tetramethylpyridyl-porphin with various counter-anions

Data from brine corrosion studies using ms-tetramethylpyridyloporphin and various counter-anions. Temperature varied between 19° and 23°. The concentration of NaCl was always 1.00% and the pH 6.

<u>Counter-anion</u>	<u>%Δm, 12 h</u>	<u>%Δm, 48 h</u>	<u>Comment</u>
Iodide	0	1.30	Samples tarnished
Chloride	0	0.0	Samples tarnished
Benzoate	0	0.79	Samples untarnished
Sulfate	0.5	2.80	Samples tarnished

(These values represent averages of at least three samples.)

Table 6
Corrosion Rates in the Presence of Metallolporphyrins
Concentration of porphyrin: 10^{-4} M

<u>Incorporated Metal</u>	<u>%Δm/12 hr</u>	<u>%Δm/48 hr</u>
Blank	0.31	0.98
VO ²⁺	0.22	0.81
Co ²⁺	0.23	0.66
Cu ²⁺	0.27	0.85
Fe ³⁺	0.12	0.26
Ni ²⁺	0.26	0.79

Table 7

The Effect of the Variation of Porphyrin Concentration and Environment on the Rate of Corrosion. Each Entry is an Average of Three Measurements.

(P)	Environment/% mass loss per 48 h		
1.1×10^{-3}	A/0.32	B/1.8	C/1.4
1.1×10^{-4}	A/0.36	B/1.7	C/1.4
1.1×10^{-5}	A/0.68	B/1.7	C/1.4
1.1×10^{-6}	A/1.38	B/1.7	C/1.6

five 24/40 (standard taper) outer member necks. Hence the cell accommodates a specimen electrode, two platinum counter electrodes, a salt bridge to the calomel electrode, and an argon gas purge system. The working surfaces of the specimen and platinum electrodes are at the same depth. A minimum volume of approximately 720 ml of solution is required to charge the cell for a polarization study.

We are using the Anotrol 4100 Potentiostat with a Fluke 8010 A Digital Multimeter as an ammeter and a Pope 1502 pH/ion meter as an electrometer. The electrometer is connected directly across the specimen and saturated calomel electrodes. The ammeter is connected in series between the platinum electrodes and the power output of the potentiostat. The polarization experiments are conducted using manual control of the applied voltage.

4.2 Procedures

All measurements are made in 2.0% aqueous NaCl solution in order to make our data directly comparable to data obtained at NADC. The system has been calibrated and tested for reproducibility by performing several polarization experiments on Type 401 stainless steel and on pure iron (John Matthey Chemicals Limited, Puratronic Iron Rod; Batch 08729). The difference between the steel and iron samples occurs during the anodic segment where, when E is more anodic than -400mv, vs SCE, the current densities for the iron electrode are higher; the current densities during the cathodic segment are the same within experimental error.

The specimen electrodes were placed in contact with the potential inhibitors in two ways: 1) In cases where the porphyrin was water soluble

(tetramethylpyridiniumporphin iodide and tetra-n-octylpyridiniumporphin iodide) a weighed amount of inhibitor was simply added to the NaCl solution. 2) In cases where the porphyrin was water insoluble the specimen electrode was immersed in a benzene solution of the porphyrin (10^{-4} M) for a period of 6 to 10 hours and dried at 100°C for 1 hour.

4.3 Results

Only water soluble porphyrins show any effect on the current densities. Unfortunately, inhibition, even with the water soluble porphyrins is not always detected: In seven experiments with tetramethylpyridylporphin iodide we noted appreciable cathodic inhibition five times and no effects twice. When inhibition is observed we see an approximate order of magnitude decrease in current densities.

When tetra(4-methylpyridyl)porphin and its various metalloderivatives are added to the corrosive environment (2.0% aqueous NaCl) we see inflections in the anodic and/or cathodic traces in almost all instances. We can be confident that these inflections are not due to oxygen reduction or oxidation/reduction of the porphyrin itself: Solutions which have been vigorously purged with Ar(g) for periods as long as 2 hours exhibit these inflections; and spectrophotometric analysis of these solutions shows that the porphyrin itself is unchanged. (We know from luminescence studies that vigorous purging of solutions with argon for 15 minutes is effective in bringing dissolved oxygen to negligible levels; also spectrophotometry is very sensitive for the detection of redox changes in porphyrins and metalloporphyrins.) Therefore, we conclude that the materials must adsorb on the iron electrode and change its surface characteristics. We

note in the case of metal-free tetra(4-methylpyridyl)porphin that there is in the majority of our experiments an appreciable reduction in cathodic current. This can be rationalized in terms of an electrostatic driving force which brings the cationic porphyrin to the iron surface where it interferes with the cathodic reaction. We do not understand why the reduction in cathodic current is not always observed.

Several of the traces obtained from these studies are presented in the following figures. The ordinate is in mV and the abscissa is the logarithm of the current density, mA/cm². Figure 2 represents typical blank runs. Pure iron and Type 401 stainless steel were studied in the absence of porphyrin inhibitors. Figures 3 through 7 represent traces using a pure iron working electrode with ms-tetra(4-methylpyridyl)porphin and its various metallo-derivatives in a 2.0% aqueous NaCl solution. The concentration of the porphyrin is about 10⁻⁴ M. The open circuit potential is usually between -550 and -626mV. The thermodynamic value for Fe/Fe²⁺ vs SCE is -677mV. Figure 8 represents the trace using tetra(4-carboxyphenyl)porphin in a slightly basic solution (pH[~]8).

In the presence of porphyrins and metalloporphyrins there is always an increase in "noise". Despite this fact, it appears that there is often a repeatable diminution of the current for a given value of the potential. We feel that the major problem in obtaining strong inhibition involves the low solubility of the porphyrins in aqueous media.

Analysis of the potentiostatic polarization data should allow us to calculate the corrosion current and the Tafel constants. From these parameters we could estimate the corrosion rates and it would be very interesting to compare these results with the corrosion rates determined directly from the mass loss

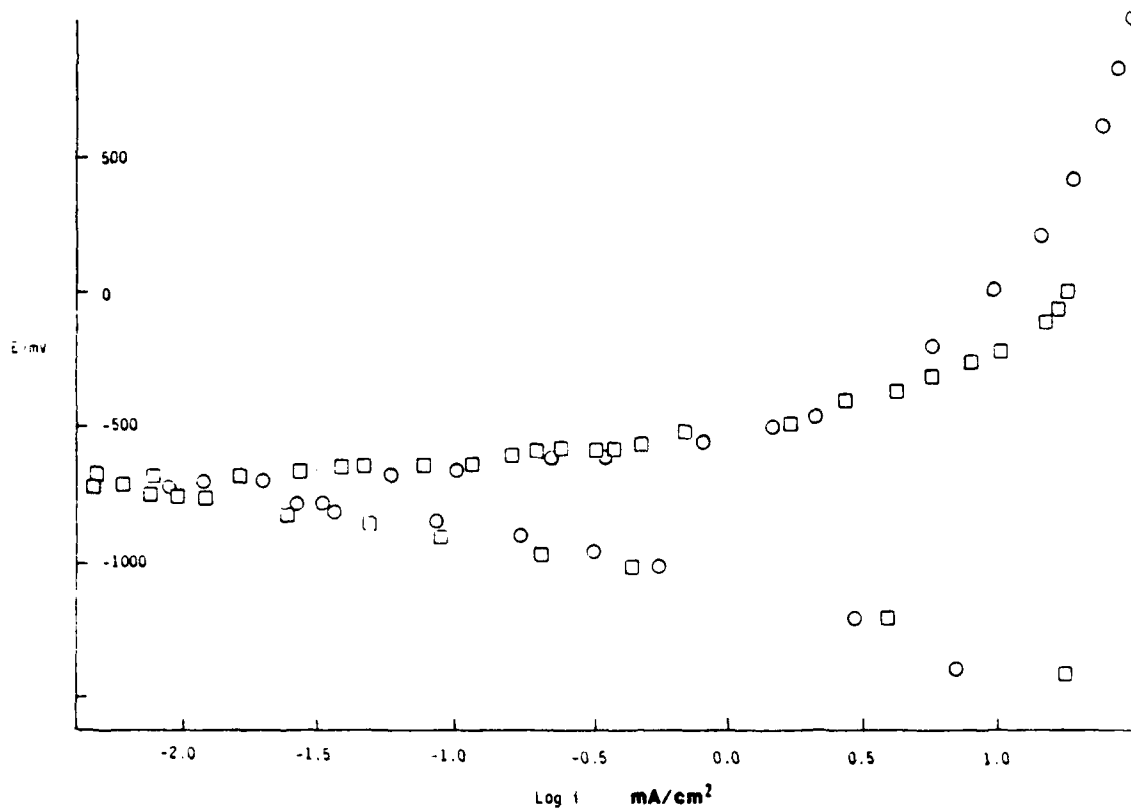


Figure 2. A comparison of the potentiostatic polarization curves using a pure iron \square working electrode and a 401 steel \circ working electrode in 2.0% NaCl(aq) with no inhibitor.

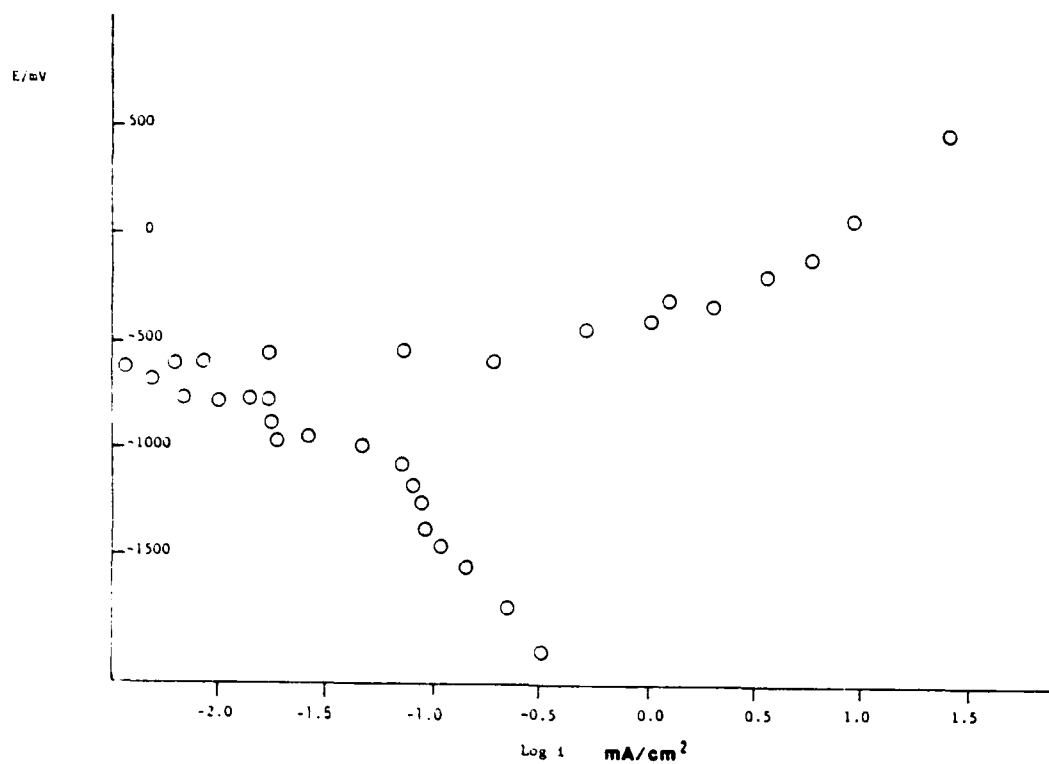


Figure 3. The potentiostatic polarization curve using a pure iron working electrode in 2.0% NaCl(aq) containing *ms*-tetramethylpyridylporphin (10^{-4} M) as an inhibitor.

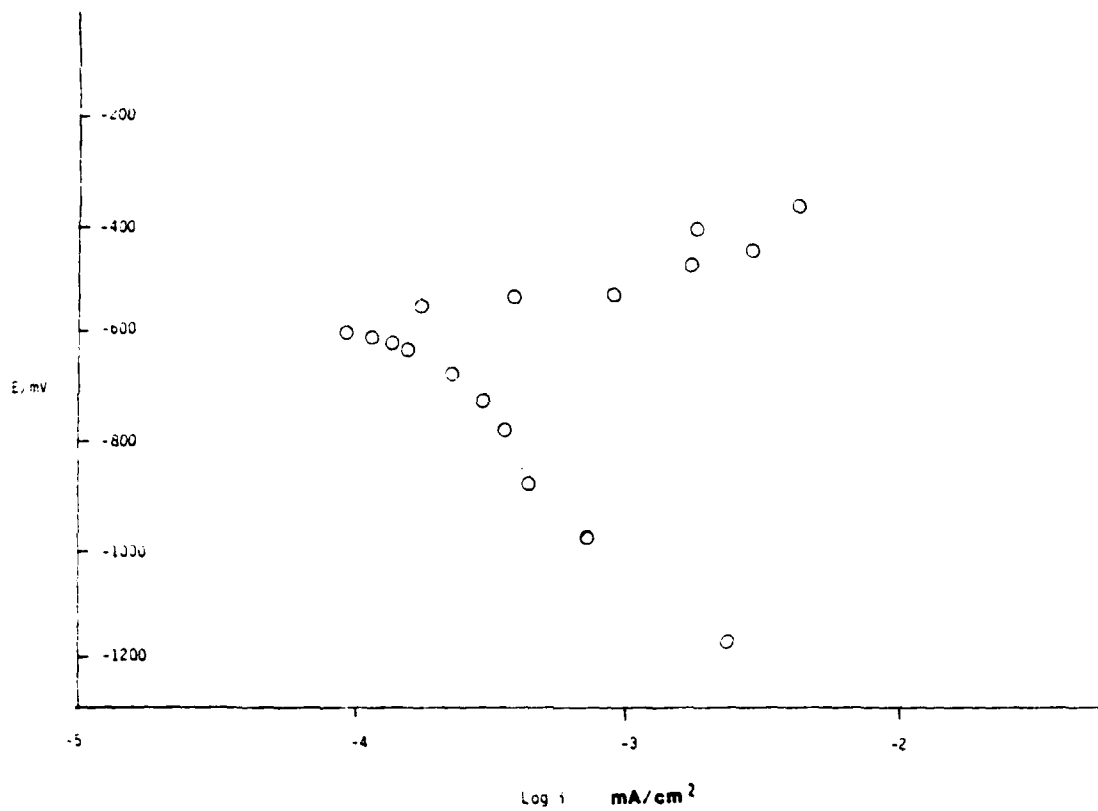


Figure 4. The potentiostatic polarization curve using a pure iron working electrode in 2.0% NaCl(aq), containing vanadyl-ms-tetramethylpyridylporphin (10^{-4} M) as an inhibitor.

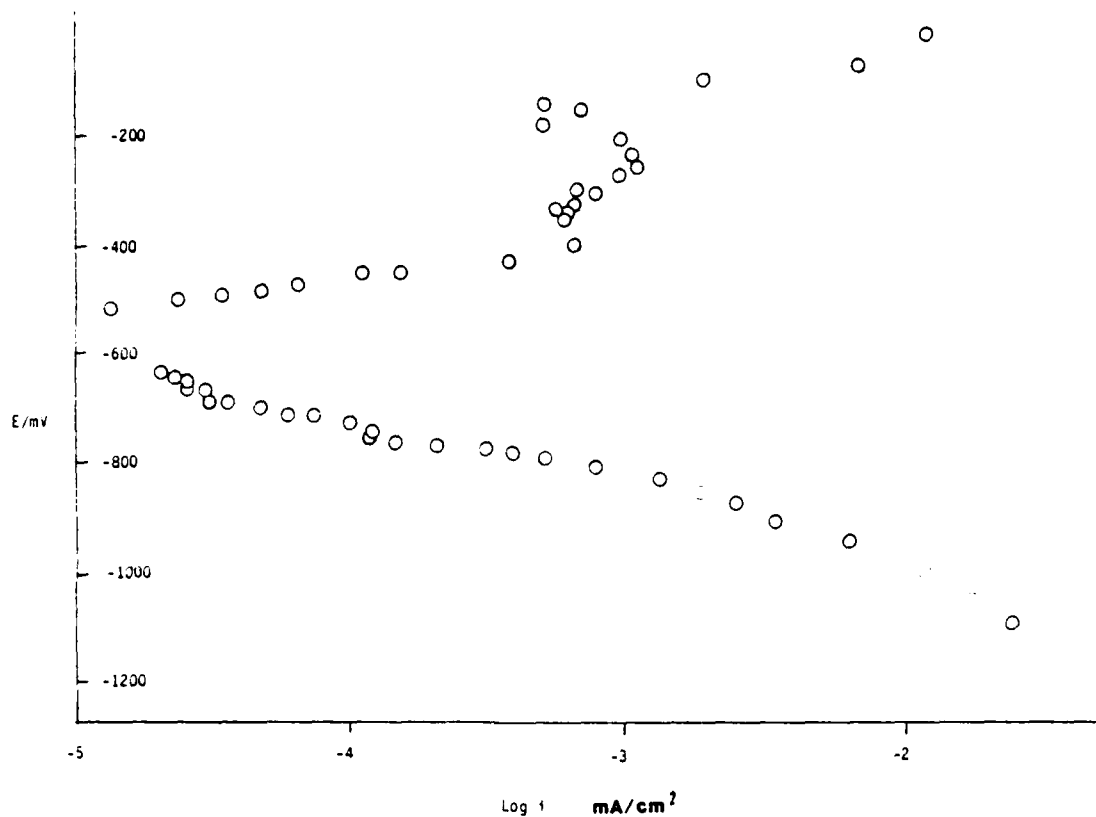


Figure 5. The potentiostatic polarization curve using a pure iron working electrode in 2.0% NaCl(aq), containing iron(III)-ms-tetra-methylpyridylporphin ($10^{-4}M$) as an inhibitor.

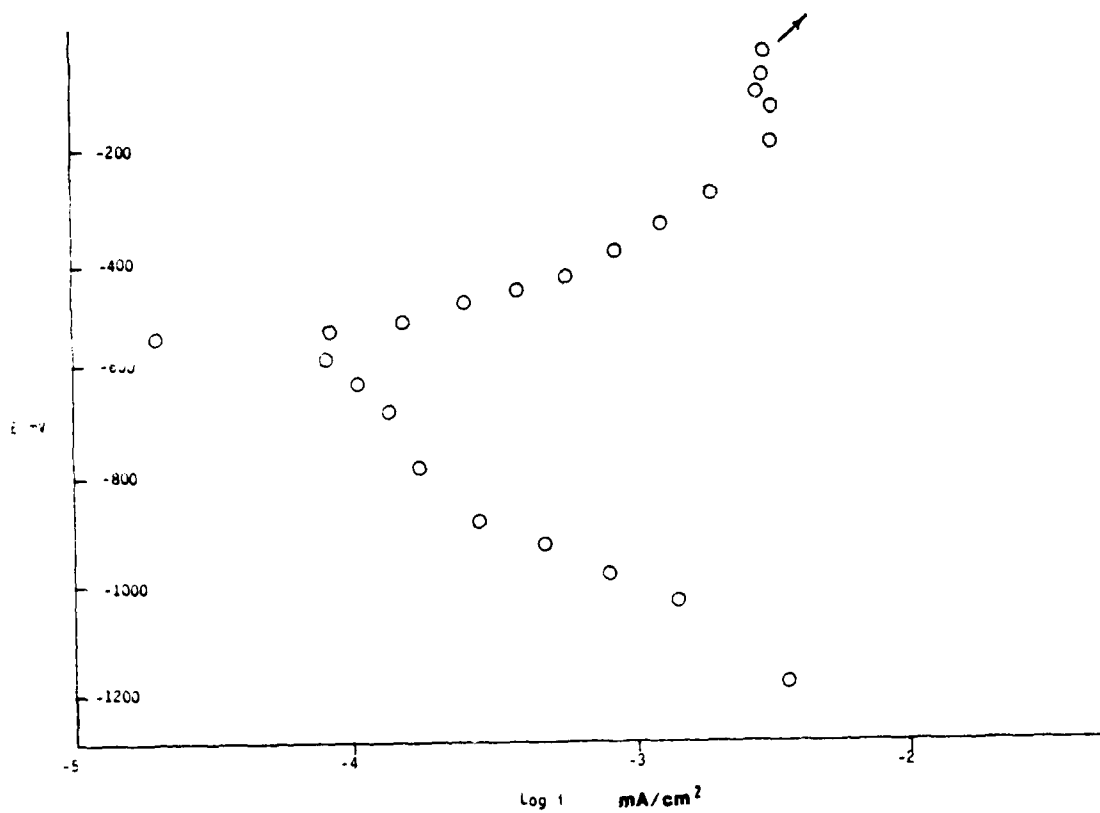


Figure 6. The potentiostatic polarization curve using a pure iron working electrode in 2.0% NaCl(aq), containing Cu(II)-ms-tetra-methylpyridylporphin (10^{-4}M) as an inhibitor.

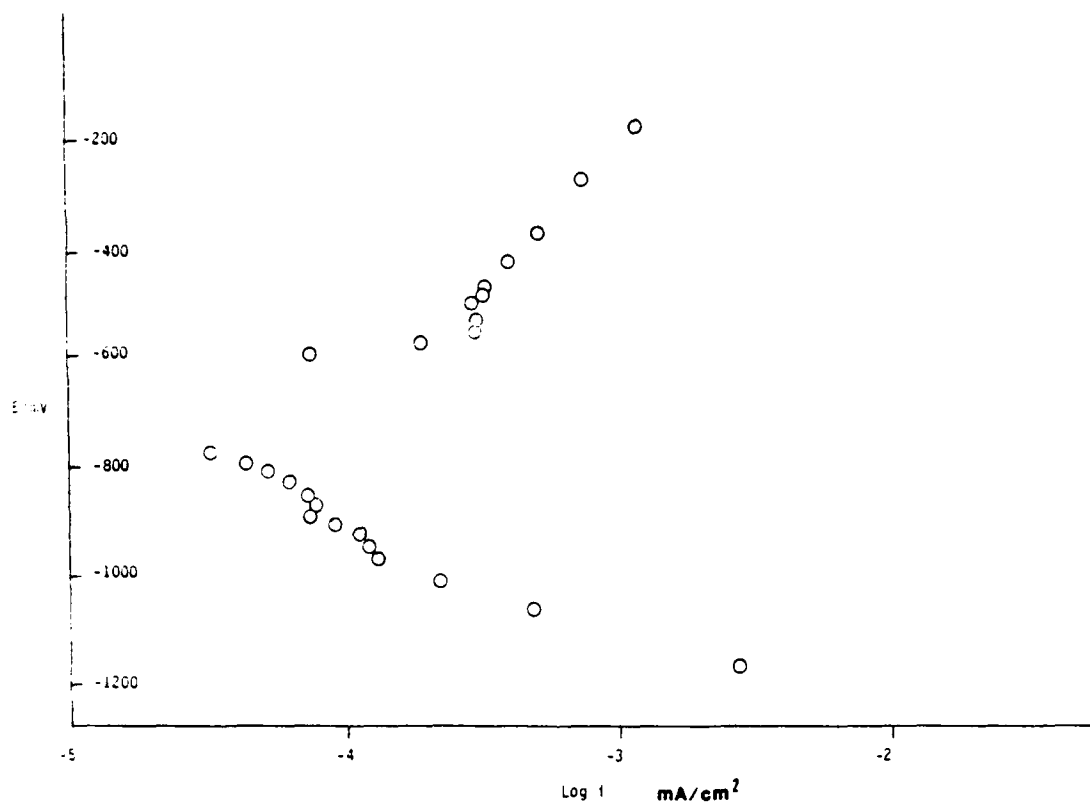


Figure 7. The potentiostatic polarization curve using a pure iron working electrode in 2.0% NaCl(aq), containing Co(II)-ms-tetra-methylpyridylporphin (10^{-4} M) as an inhibitor.

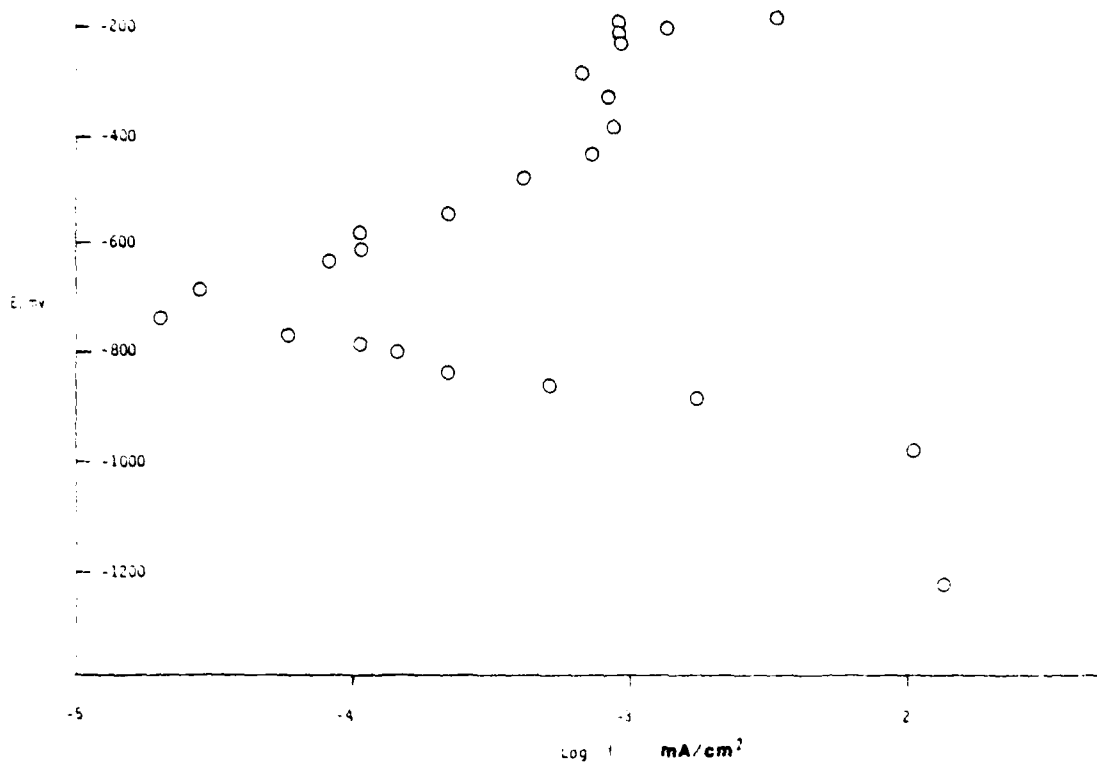


Figure 8. The potentiostatic polarization curve using a pure iron working electrode in 2.0% NaCl(aq), containing ms-tetracarboxyphenylporphin (10^{-4} M) as an inhibitor.

experiments. However, because of the uncertainties in the measured values of the current, especially at low current, a quantitative analysis of the data and a comparison of the results were not possible.

5.0 DISCUSSION

The greatest fraction of our effort has been devoted to the synthesis of porphyrins which we believe have high potential as corrosion inhibitors. Physical studies on these materials lead to the conclusion that a) in order to see strong inhibition from porphyrinic materials we must synthesize materials which have a much higher water solubility and b) it is probable that metallo-porphyrins are stronger inhibitors than free-base porphyrins.

Our mass-loss immersion and potentiostatic polarization studies are good tests of inhibition but the larger size of the electrodes in the potentiostatic studies leads to scans in which the E vs $\log i$ traces are not strictly reproducible. Therefore, we have designed smaller spinning iron electrodes (diam 1 mm) which we intend to use in polarographic and cyclic voltammetric studies. We hope to be able to measure the effect of porphyrins (absorbed on the surface of the iron electrode) on the reduction and oxidation potentials of iron.

The structures which we feel will almost certainly give appreciable inhibition are metallo-derivatives of 5,10,15,20-tetra(1,3-dimethyl-5-pyrimidyl) porphin. It carries a charge of +8 and should show strong interactions with cathodic sites. We have prepared small amounts of this material but so far the percentage yield from our synthesis is very low.

In the next quarter we shall devote more of our time to the collecting of polarographic data; and also we shall submit porphyrin treated samples of iron

foil for electron microscope analysis.

6.0 ACKNOWLEDGEMENTS

The following students participated in the research. Louis R. Nudy, Ph.D. Candidate; Cherylann Schieber, Undergraduate; Howard G. Hutchinson, Undergraduate; Francine Douwes, Undergraduate; Joan Coffey, Undergraduate.

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8.0 APPENDIX

Document 1: On the Aromaticity of Porphin, L. R. Nudy,
C. C. Coffey, F. R. Longo and J. B. Kim, J. Heterocyclic
Chem. 19 1589 (1982)

Document 2: A Study of Bromoporphins, L. R. Nudy, H. G.
Hutchinson, C. Schieber and F. R. Longo, Tetrahedron 40
2359 (1984)

Nov-Dec 1982

On The Aromaticity of Porphin

1589

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We have undertaken a study of the bromination of porphin. We have learned contrary to literature reports, that bromine (in chloroform) attacks porphin preferentially at the meso position and that bromination of this meso monobromoporphin produces a single dibromo product, namely 5, 15-dibromoporphin. Our results are interpreted in terms of the aromaticity of the different peripheral carbon atoms.

J. Heterocyclic Chem., 19, 1589 (1982).

The bromination of porphin and other porphyrins has been studied by several groups (1-5). All these workers report that attachment of bromine occurs at the pyrrole

positions. For instance, Caughey, Alben, Fujimoto, and York (1) studied the bromination of the dimethyl ester of deuterioporphyrin IX and found that substitution occurs at the pyrrole positions, producing the 3,8-dibromo derivative. Samuels, Shuttleworth, and Stevens (2) report that the bromination of porphin by reaction of bromine in chloroform or *N*-bromosuccinimide in carbon tetrachloride yields a single product, β -monobromoporphin. Schlozer and Fuhrhop (3) confirmed the report of Samuels *et al.* Bonnett, Gale, and Stephenson (4) have reported that direct bromination of octaethylporphin fails. Hence, all

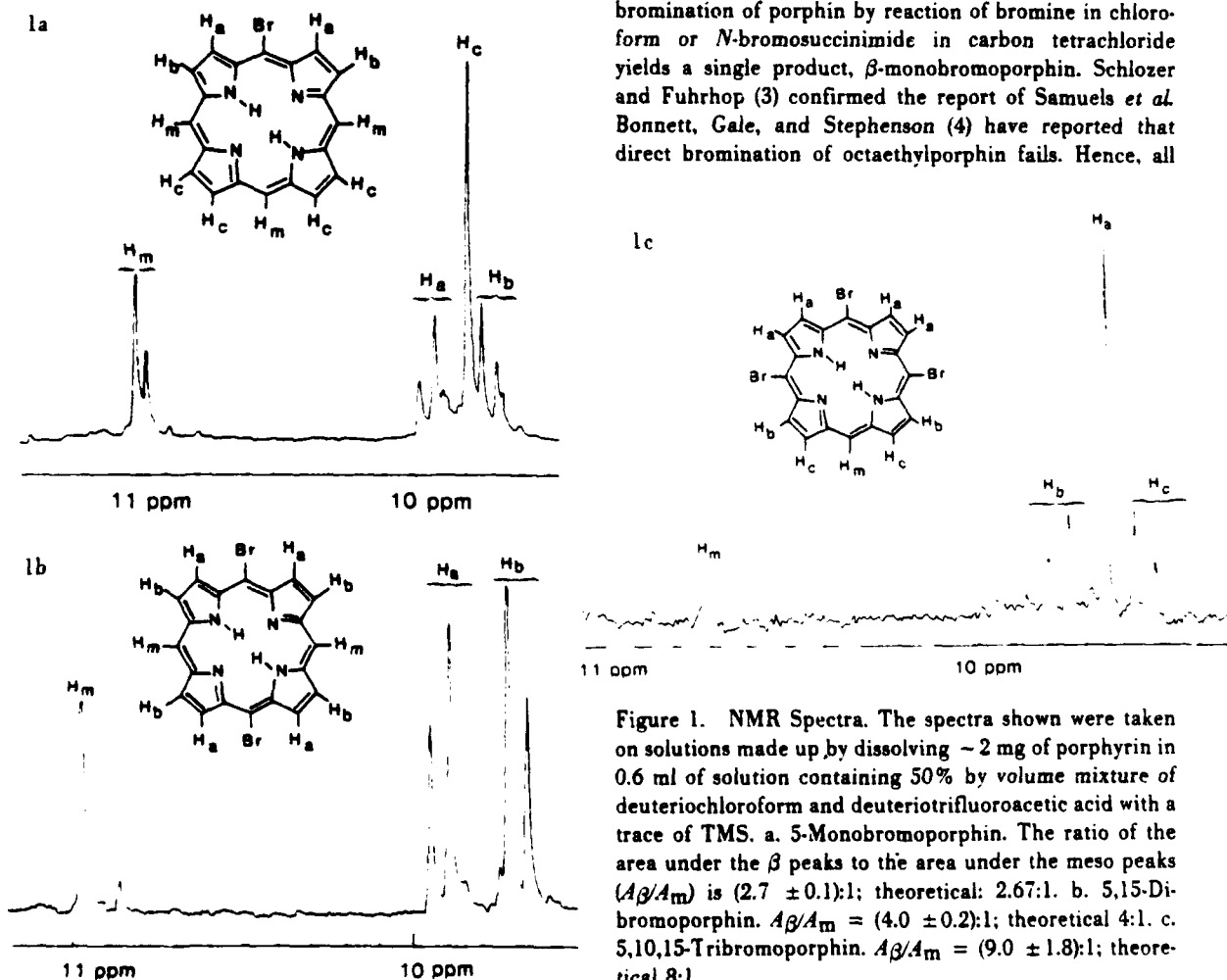


Figure 1. NMR Spectra. The spectra shown were taken on solutions made up by dissolving ~ 2 mg of porphyrin in 0.6 ml of solution containing 50% by volume mixture of deuteriochloroform and deuteriotrifluoroacetic acid with a trace of TMS. a. 5-Monobromoporphin. The ratio of the area under the β peaks to the area under the meso peaks (A_{β}/A_m) is $(2.7 \pm 0.1):1$; theoretical: 2.67:1. b. 5,15-Dibromoporphin. $A_{\beta}/A_m = (4.0 \pm 0.2):1$; theoretical 4:1. c. 5,10,15-Tribromoporphin. $A_{\beta}/A_m = (9.0 \pm 1.8):1$; theoretical 8:1.

reports in the literature indicate that bromination of the pyrrol position is favored over the meso position. This work is significant in terms of the aromaticity of the porphyrin nucleus.

On the basis of our earlier results on the nitration of porphin (6) we joined the school which holds that the inner cycle of 16 atoms and 18π electrons is the aromatic part of the porphyrin molecule and that the β - β bonds in the residues are more olefinic in nature. The reported bromination at the pyrrol position would not be inconsistent with our point of view provided the bromination proceed via addition-elimination. Our experiments, which were designed to test this hypothesis, all failed. We did not obtain β -monobromoporphin when we treated porphin with bromine in chloroform or in acetic acid. The chloroform reaction yielded at least three products (I, II, III); the acetic acid reaction yielded at least six products, only three of which were produced in appreciable amounts. The three major products of the acetic acid preparation are identical with the three bromoporphins obtained in the chloroform preparation.

All porphyrins were separated and purified by repeated chromatography on dry, acidic alumina. They were then re-crystallized from 50v:50v hexane-benzene solutions. Compound I has a visible spectrum identical to that reported by Samuels, *et al.* for the product which they identified as β -monobromoporphin. The mass spectra (Finnegan

4021 GS/MS/DS System) of compounds I, II, and III showed that they were a mono-, a di-, and a tribromoporphin, respectively. The nmr (Joel FX 90Q/EM/LPCS) spectra showed that I is 5-monobromoporphin, II is 5,15-dibromoporphin, and III is 5,10,15-tribromoporphin. (See Figures 1a, b and c.) These results strongly suggest that the bromination of porphin is electrophilic, that a bromine substituent on a porphin nucleus has a very strong and predictable directing effect (since only a single dibromo structure was formed in any appreciable amount), and that only the methine bridge positions are chemically benzene-like, i.e., aromatic.

We wish to thank Dr. J. E. Drach for enlightening discussions and helpful suggestions and we gratefully acknowledge the support of the Naval Air Development Center (Contract No. N62269-81-C-0278) at Warminster, PA.

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A STUDY OF BROMOPORPHINS

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(Received in USA 12 December 1983)

ABSTRACT - The synthesis and characterizations of 2-bromoporphin, 5-bromoporphin, 5,15-dibromoporphin, and 5,10,15-tribromoporphin are described. Yields of the bromoporphins obtained with a variety of brominating agents are reported. Spectral properties were measured and, along with chemical properties, are presented as evidence for a preferred delocalization pathway in porphin.

INTRODUCTION

There have been several recent publications which deal with question of the preferred path of delocalization of the π -electrons, in the porphyrin structure. Some studies support the inner β membered dianion while other studies support a system which includes the peripheries of opposite pyrrole residues. The bases of these arguments lie in ^{13}C -NMR (1,2), ^1H -NMR (3,4,5), crystallographic, (6) theoretical (7), and chemical studies (8).

In this manuscript we describe a study of the bromination of the parent compound porphin. We feel that the work supports the hypothesis originally proposed by Fleisner and Webb that the pathway of π -electron delocalization does not include the β -carbon atoms of the pyr. residues.

Electrophilic substitution on porphyrins generally leads to products which are meso rather than beta substituted. Several recent reviews of such reactions contain numerous examples which confirm this general selectivity. (9,10,11) One notable exception to this general trend is the previously reported bromination of porphin. Samuels, Shuttleworth, and Stevens reported that bromination of porphin with molecular bromine in chloroform gives 2-bromoporphin, exclusively. (12) A consideration of the Fleisner-Webb hypothesis (13), that the beta pyrrol positions of the porphyrin moiety are somewhat olefinic, suggests that the formation of the 2-bromoporphin may result from Br_2 addition followed by HBr elimination. We attempted to test this idea but, surprisingly, all attempts to form 2-bromoporphin by direct bromination of porphin failed. The synthesis and characterization of the various bromoporphins obtained in this study are reported in this paper.

EXPERIMENTAL

Visible absorption spectra were measured at room temperature in spectral grade solvents with the Perkin Elmer Model 520 Spectrophotometer. Spectral data for all of the new porphyrins reported in this paper are given in Table 1. Fluorescence spectra were measured with the Spex Fluorolox 222 equipped with a 450 W xenon lamp and photon counting capability; all solutions whose fluorescence was examined had optical densities of approximately 0.04 at band IV. The NMR spectra were taken on a Joel FT 90Q; we have previously communicated the NMR spectra of 5-bromoporphin, 5, 15-dibromoporphin, and 5, 10, 15-tribromoporphin. (14) Due to the low solubility of 2-bromoporphin we

were forced to use highly deuterated chloroform (99.96% atom purity) to obtain its NMR spectrum. Mass spectra were recorded with the Finnegan 4021 GS/MS/DS System and the HP 5995 GC/MS System.

5,10,15-tribromoporphin To a 5-liter flask equipped with stirrer and condenser was added 90 mg of porphin and two liters of 90% acetic acid in water at room temperature. When all the porphin had dissolved an equimolar quantity of bromine in 30 ml of the same solvent was added dropwise over a period of 5 minutes. Stirring of the solution was continued for two hours at which point the solvent was removed by rotoevaporator. The red solid was redissolved in benzene and chromatographed on a column (5cm x 120cm) packed with 4 kg of dry neutral alumina (Brockman Activity I). After elution with benzene four major bands were apparent. The three bands which were eluted first did not fluoresce. Significant broadening of these bands occurred as they moved down the column. The first band, which moved close to the solvent front, was concentrated and allowed to crystallize from a solution of 50v:50v, hexane-benzene. The red crystals were washed with cold hexane. The mass spectrum revealed a base peak at 548 m/e. The ratio of peak heights at 544, 546, 548 and 550 m/e was 1:3.1:3.5:1.0. Taking into account only bromine isotope effects, the mass ratio expected for a tribromo compound is 1:3:3:1. The components of the next three bands in order of elution were identified as follows; 5,15-dibromoporphin, 5-bromoporphin and porphin, respectively. 5-bromoporphin and 5,15-dibromoporphin can best be prepared with other reagents (*vide infra*).

TABLE 1: Visible Absorption Data

Porphyrin	Wavelength in nm (extinction coefficients x 10 ⁻³)				
	Soret	IV	III	II	I
5, 10, 15 - Tribromoporphin	417(217)	518(13.2)	551(7.6)	600(4.1)	657(3.2)
5, 10 - Dibromoporphin	415(238)	508(12.7)	540(7.6)	586(4.0)	640(2.5)
5 - Bromoporphin	402(242)	495(14.3)	525(2.9)	572(4.4)	625(0.59)
2 - Bromoporphin	398(246)	492(16.3)	522(5.2)	563(5.8)	616(0.83)
Porphin (9)	395(261)	490(16.0)	520(3.0)	563(5.2)	616(0.89)

TABLE 2: BROMINATIONS OF PORPHIN

REAGENT	PERCENT RECOVERY		
	PORPHIN	5-BROMOPORPHIN	5,15-DIBROMOPORPHIN
Molecular Bromine	24	54	15
Pyridinium Bromide Perbromide	31	53	15
N-Bromo succinimide	20	71	8

5-Bromoporphin and 5,15-Dibromoporphin The 5-bromoporphin and the 5,15-dibromoporphin can be isolated as products of the reaction of porphin with molecular bromine in CHCl₃, with pyridinium bromide perbromide in CHCl₃, or with N-bromosuccinimide in CHCl₃. Yields of porphyrins obtained with each of the different brominating reagents are reported in Table 2. In all cases an equimolar amount of brominating agent in solution is added over a 5 minute period to a stirred solution of porphin in the same solvent at 20-50°C. The concentration of porphin was of the order of 10⁻⁴M. Reaction is quenched after another 5 minutes by addition of an excess amount of acetone. The solution is then washed with water, dried over anhydrous sodium sulfate, filtered, and evaporated to dryness to yield a red solid. Flash chromatography on silica gel (40 μ average particle diameter, supplied by Baker) with a 33v:67v hexane-toluene eluent was found to be more practical than separation on alumina. In this method two non-fluorescent bands elute first; the first band proved to be 5,15-dibromoporphin and the second, 5-bromoporphin.

The first band was concentrated and recrystallized from 50v:50v hexane-benzene producing a red solid which has a base peak in its mass spectrum at 468 m/e. The intensities of peaks at 466, 468 and 470 m/e were found in the ratio of 1:2.2:1.2; (expected ratio for dibromoporphin: 1:2:1). The NMR spectrum in a 50% by volume mixture of CDCl₃ and CF₃COOD showed a meso peak at 10.9 ppm from TMS and a symmetrical beta multiplet centered at 9.8 ppm. The beta to meso area ratio observed was (4.0 0.02):1; (expected for 5, 15-dibromoporphin: 4:1).

The second non-fluorescent band was isolated and recrystallized in the same fashion. The mass spectrum revealed two peaks at 388 and 390 m/e with a relative abundance of 98 and 100% respectively; expected for 5-bromoporphin: 1:1. The NMR showed a meso peak at 11 ppm and a symmetrical beta multiplet at 9.9 ppm. The beta area to meso area ratio was found to be (2.7 0.1):1 (expected for 5-bromoporphin: 2.67:1).

2-Bromoporphin A stirred solution containing 0.6 g of 4-bromo-2-methylpyrrole (0.007 mol), obtained by the method of Anderson and Lee, (15) and 0.94 g of 2-methylpyrrole (0.009 mol), obtained by the method of Sliverstein, Ryskiewicz, and Chaikin (16) was maintained at 100°C for 24 hours. At this point the solution was cooled, filtered and evaporated to dryness on a

rotoevaporator. The resulting red solid was then dissolved in a 33v:67v heptane-toluene solution and flash chromatographed on silica gel. Two major bands, both of which fluoresce were collected and found to be porphin and 2-bromoporphin; the latter was eluted first. Spectroscopic yields of the major components were determined using Soret extinction coefficients. We obtained approximately 0.4% yield of 2-bromoporphin with a 0.6% recovery of porphin. Porphin was identified by its visible absorption spectrum. The 2-bromoporphin was identified by mass spectrometry, which gave the appropriate doublet of peaks at 388 and 390 m/e corresponding to the expected molecular ions and by NMR in deuteochloroform which revealed three peaks in the meso region centered at 10.5 ppm and a complex multiplet in the beta region centered at 9.6 ppm. The beta to meso area ratio was 1.8:1 (expected for a 2-bromoporphin 1.75:1). Figure 1 is a comparison of the NMR spectra of 5-bromo and of 2-bromoporphin.

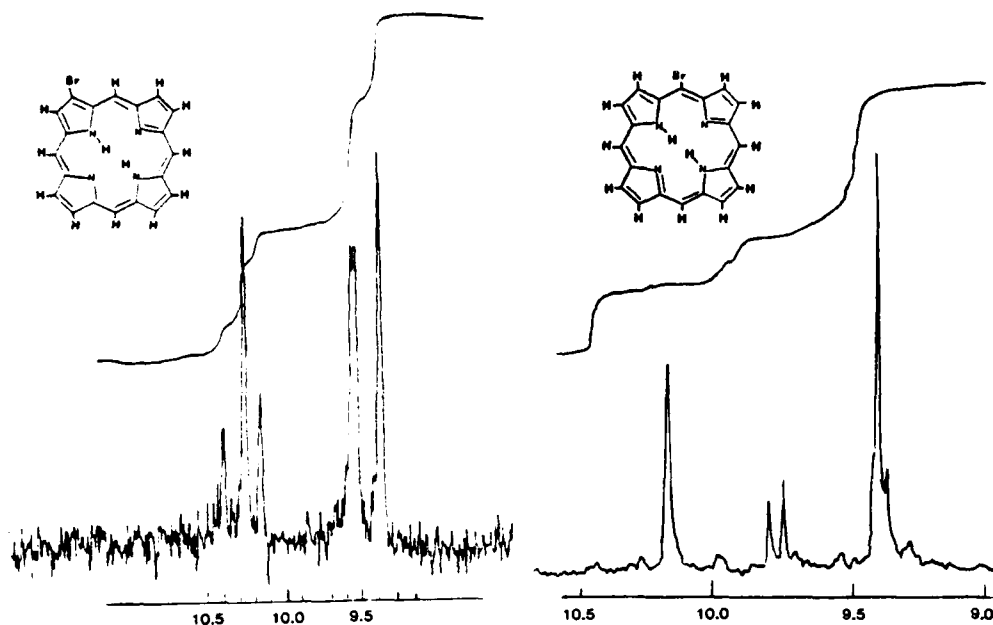


Figure 1. Proton NMR spectra of 2-bromoporphin and 5-bromoporphin in 99.96% deuterated CHCl_3 .

RESULTS AND DISCUSSION

The Fleischer-Webb (F-W) model in which the aromaticity does not extend to the beta pyrrol positions permits the explanation of meso nitration (17) and formylation (18) as ordinary electrophilic aromatic substitution. Initially, we devised experiments to determine the mechanism of bromination, which according to the literature, resulted in beta attack only, yielding 2-bromoporphin (12) and therefore did not appear to be in accord with the F-W Model. Beta-bromination would conform to the F-W Model provided that it take place via an addition-elimination reaction involving a β -pyrrol bond. Experiments devised to test this possibility were negative; we found that bromination of porphin can be detected only at the meso positions under the conditions of our experiments. Our observations are in agreement with the observations of Callot and Schaeffer (19) who briefly investigated the bromination of porphin in order to evaluate the competition between meso and beta-pyrrol carbon atoms. The results of our studies with different brominating systems are presented in Table 2; note that the yield of 5-bromoporphin by bromination with N -bromosuccinimide is quite high. In no case were we able to detect beta brominated species as reported by Samuels, et. al.

Indeed faint bands were noticed during the chromatographic separation of the porphyrin products of these reactions. The small yields of these materials precluded structural analysis but the presence of 2-bromoporphin can probably be ruled out: These faint bands were eluted after porphin whereas 2-bromoporphin has a greater R_f than porphin under the same conditions. We estimate

using a molar absorptivity of 2×10^5 in the Soret region that the total yield of porphyrins in these bands is less than 1%. These bands were fluorescent and the visible spectra were different from the spectra of the structures which we have identified.

Of the two possible meso dibromo porphyrins only 5,15-dibromoporphyrin was detected in our product mixtures. Since the dibromo species is produced from 5-bromoporphyrin it is obvious that the bromo-substituent at the meso position exhibits a predictable directing effect (20). We have now demonstrated that bromo, nitro, and N-acetylamino groups, substituted at the meso position of porphyrin, direct the next substitution in a predictable manner and we conclude that the electrophilic substitution studies on porphyrin (6, 9, 11, 13) support the F-W model.

The trends in the visible absorption and fluorescence data for the bromoporphyrins can be explained in terms of the F-W model also. The effect of a bromine substituent on the optical properties of the porphyrins is shown in Table 1. Listed are the absorption maxima and molar absorptivities for the porphyrins which we have synthesized. These data demonstrate that the bonding of a bromine atom to a peripheral position results in bathochromic shifts of absorption maxima and diminutions of the Soret molar absorptivities. Both of these effects are much smaller for 2-bromoporphyrin than for 5-bromoporphyrin. The shifts and diminutions increase with increasing meso-bromination.

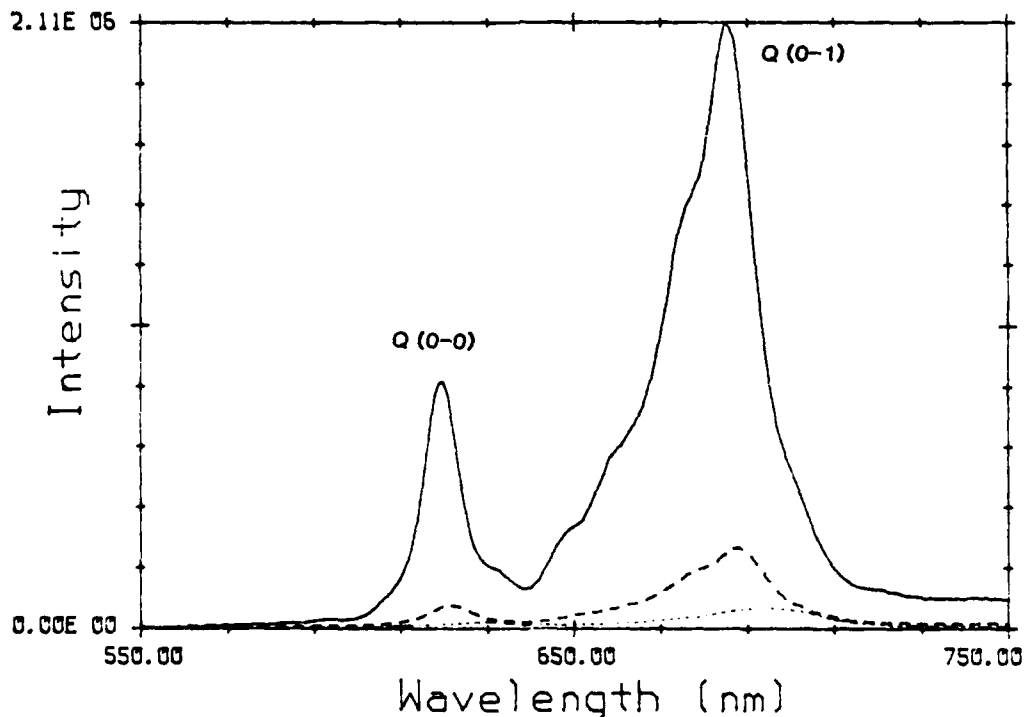


Figure 2. Fluorescence spectra: porphyrin indicated by solid line, 2-bromoporphyrin by dashed line, and 5-bromoporphyrin by dotted line.

The corrected fluorescence spectra of porphyrin, 2-bromoporphyrin, and 5-bromoporphyrin are shown in Figure 2. Considering the Q(0-0) transition which occurs at 625 nm, it appears that the intensity of fluorescence for porphyrin is 10 times greater than that of 2-bromoporphyrin and 50 times greater than that of 5-bromoporphyrin. Gouterman and Khalil (21) have examined the effect of bromine and iodine on the luminescence of various metal free porphyrins. They found that the fluorescence intensity of mesoporphyrin IX dimethyl ester in EPA (ethyl ether: isopentane: ethanol in a volume ratio of 5:5:2) was 7 times greater than the fluorescence from a solution which was 90 EPA/10 ethyl iodide and 72 times greater than from a solution which was 25 EPA/75 ethyl iodide. It appears, considering the fact that the atomic spin-orbit coupling constant for I is 5.4 times greater than that for Br, that a bromine atom bonded to a beta position on the porphyrin periphery is no more effective a quencher than

an external heavy atom.

Our studies of the bromoporphins continue to demonstrate that it is possible with the F-W model to predict and explain the chemical and physical properties of the parent porphyrin.

Acknowledgements: We wish to thank Drs. J.E. Drach and D.J. Quimby for helpful suggestions during the course of these investigations. The work was partially supported by the Naval Air Development Center (Contract No. N62269-81-C-0778) at Warminster, Penna.

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58